

STRONTIUM SORPTION STUDIES
ON CRANDALLITE

By Irving May, Marian M. Schnepfe, and Charles R. Naeser

UNITED STATES DEPARTMENT OF THE INTERIOR
GEOLOGICAL SURVEY

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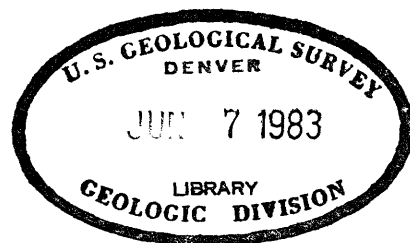
Irving May, Marian M. Schnepfe,
and Charles R. Naeser

June 1960

Report TEI-819

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STRONTIUM SORPTION STUDIES ON CRANDALLITE

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ABSTRACT

Crandallite ores may be useful in the treatment of nuclear waste solutions because of their reactivity with strontium in weakly acid solutions and in alkaline solutions containing aluminum.

The exchange capacity of the crandallite sample studies is not very high, being 6-10 milliequivalents of strontium and 2 milliequivalents of cesium per 100 grams of active phosphatic material. However, strontium removal is many times more effective from alkaline solutions, precipitation being the dominant mechanism. The removal of strontium is even more complete in alkaline solutions containing aluminate ions.

INTRODUCTION

The interaction of crandallite with strontium solutions was studied in the laboratory in order to evaluate its possible use as a scavenging agent for strontium-90 in waste solutions resulting from the reprocessing of reactor fuel elements.

Ames (1960) has studied the removal of strontium from solution by a replacement reaction in which apatite is formed in the interaction of alkaline phosphate solutions with calcite. Thomas and others (1960) have reported studies of the sorption of strontium on vermiculite, variscite ($\text{Al}(\text{OH})_3\text{H}_2\text{PO}_4$), Tennessee rock phosphate, and Florida pebble phosphate.

Crandallite is a hydrated basic phosphate of calcium and aluminum. Its formula, $\text{CaAl}_3(\text{PO}_4)_2(\text{OH})_5 \cdot \text{H}_2\text{O}$, corresponds to minerals having the alunite-type structure, $\text{A}^+\text{B}_3^{+3}(\text{SO}_4)_2(\text{OH})_6$. The enrichment of strontium in minerals having the alunite structure and more particularly in crandallite has been reported (Fronde1, 1958a, b). Where it is not an essential constituent, as in goyazite, as much as 3 percent SrO may be found.

Large deposits of crandallite are described by Altschuler, Jaffe, and Cuttitta (1956) in a zone of aluminum phosphate overlying the commercially mined apatite deposits of the Pliocene Bone Valley Formation in west-central Florida. This zone contains quartz, millisite $[(\text{NaK})\text{CaAl}_6(\text{PO}_4)_4(\text{OH})_9 \cdot 3\text{H}_2\text{O}]$, wavellite $[\text{Al}_3(\text{OH})_3(\text{PO}_4)_2 \cdot 5\text{H}_2\text{O}]$, in addition to crandallite. As it is derived from supergene alteration of the apatite deposit, its composition varies with depth.

The rock of the aluminum phosphate zone is friable, porous, and highly leached. It is thus readily amenable to beneficiation, as the reactive phosphatic fraction can be crushed easily and separated from the coarser quartz.

These deposits are of economic interest because the aluminum phosphate zone extends over several hundred square miles and has an average thickness of 6-7 feet. The known reserves of these deposits of which crandallite is a major mineral exceed 800 million tons (Altschuler and others, 1956). Several million tons of the aluminum phosphate zone rock are stripped annually in mining the calcium phosphate deposits.

Crandallite is of special interest as a scavenging agent for strontium because it is more resistant to solution by dilute mineral acids than most phosphate minerals and, unlike apatite, it is insoluble in alkaline and in carbonated ground waters.

Crandallite deposits thus provide a stable, cheap, and commercially available material for possible use in the removal of strontium from nuclear waste solutions.

The work was undertaken by the Geological Survey in cooperation with the Division of Reactor Development of U. S. Atomic Energy Commission as a part of a study of nuclear-waste disposal.

MATERIAL USED

The material studied was a sample of crandallite ore from the Pliocene Bone Valley Formation of Homeland, Florida. The sample had been studied previously (oral communication, Z. S. Altschuler, U. S. Geological Survey), and was known to contain major quartz and crandallite, subordinate millisite, and minor (1-5 percent) quantities of apatite, goethite, and kaolinite. This sample is closely related in petrographic character and in mineral composition to material from the middle strata of the leached zone studied by Altschuler (1956, p. 501). A spectrographic check by Helen Worthing, U. S. Geological Survey, showed the presence of 0.07 percent strontium and less than 0.003 percent cesium. The chemical analysis of this sample is given in table 1.

Quartz was isolated and determined to be 41 percent by Talvitie's (1951) procedure in which the sample is heated for 20 minutes with phosphoric acid at 250°C to dissolve minerals other than quartz. A microscopic examination of the isolate showed it to be almost pure quartz with an occasional grain of zircon. The amount of quartz agrees reasonably well with the total silica content of 46 percent. The fact that phosphoric acid does slightly attack quartz may cause the SiO_2 to be low by 2+ percent for a sample of this particle size.

Table 1.--Chemical analysis of crandallite ore

(Analysis by chemists of the U. S. Geological Survey using the methods of Shapiro and Brannock, 1956)

	<u>Percent</u>
SiO_2	46.9
Al_2O_3	18.3
Fe_2O_3	2.0
FeO	0.06
MgO	< 0.10
CaO	5.9
Na_2O	0.56
K_2O	0.18
H_2O	9.7
TiO_2	0.65
P_2O_5	15.8
MnO	0.03
CO_2	<u>0.3</u>
	100.5

Calculations based on the chemical analysis of the sample and on the theoretical formulas of the minerals give the following mineralogical composition:

	<u>Percent</u>
Quartz	41
Crandallite	34
Millisite	15
Apatite	2
Others	8

STUDIES OF STRONTIUM SORPTION

Column experiments

All column studies were made with 12-mm diameter glass columns (fig. 1) the lower parts of which were immersed in a constant temperature water bath. Flow rates were regulated by manipulating the stopcock or by applying nitrogen pressure to the head of the column. Asbestos mats served as column supports.

A preliminary sorption experiment was made with a 12-mm diameter column containing 40 grams of a +35 mesh fraction of sample gently crushed to pass 20 mesh. A strontium solution containing 100 μg Sr/ml with a few drops of free nitric acid and spiked with approximately 0.08 μC /ml of strontium-89 was passed through the sample at room temperature by gravity flow averaging 10 ml/hr. The eluate was collected in 10 ml fractions. The pH of the eluate was 6.6 which is close to the equilibrium pH of 6.3 for the sample.

The concentration of strontium in each of the fractions was determined with a Geiger-Müller counter by counting the beta activity of one-milliliter aliquots evaporated in aluminum planchets. The feed solution gave counts approximately 500 times the background level of 20 counts per minute. The experiment was discontinued after 380 ml of eluate were collected.

A well-defined break-through curve (fig. 2) was obtained, the break-through capacity (strontium uptake prior to the first detectable strontium in the eluate) being 1.54 meq Sr/100 grams.^{1/} For a symmetrical break-through curve under these conditions, a total capacity of 1.8 meq Sr/100 grams is indicated from the point where the ratio of the concentration of strontium in the eluate to the initial concentration (C/C_0) equals 0.5 (Samuelson, 1953). At the conclusion of the experiment a C/C_0 value of only 0.8 was attained with indications of some levelling of the curve; the total strontium uptake was 1.9 meq Sr/100 grams.

^{1/} Unless otherwise indicated, all capacities are calculated on the basis of the crandallite sample including natural associated quartz.

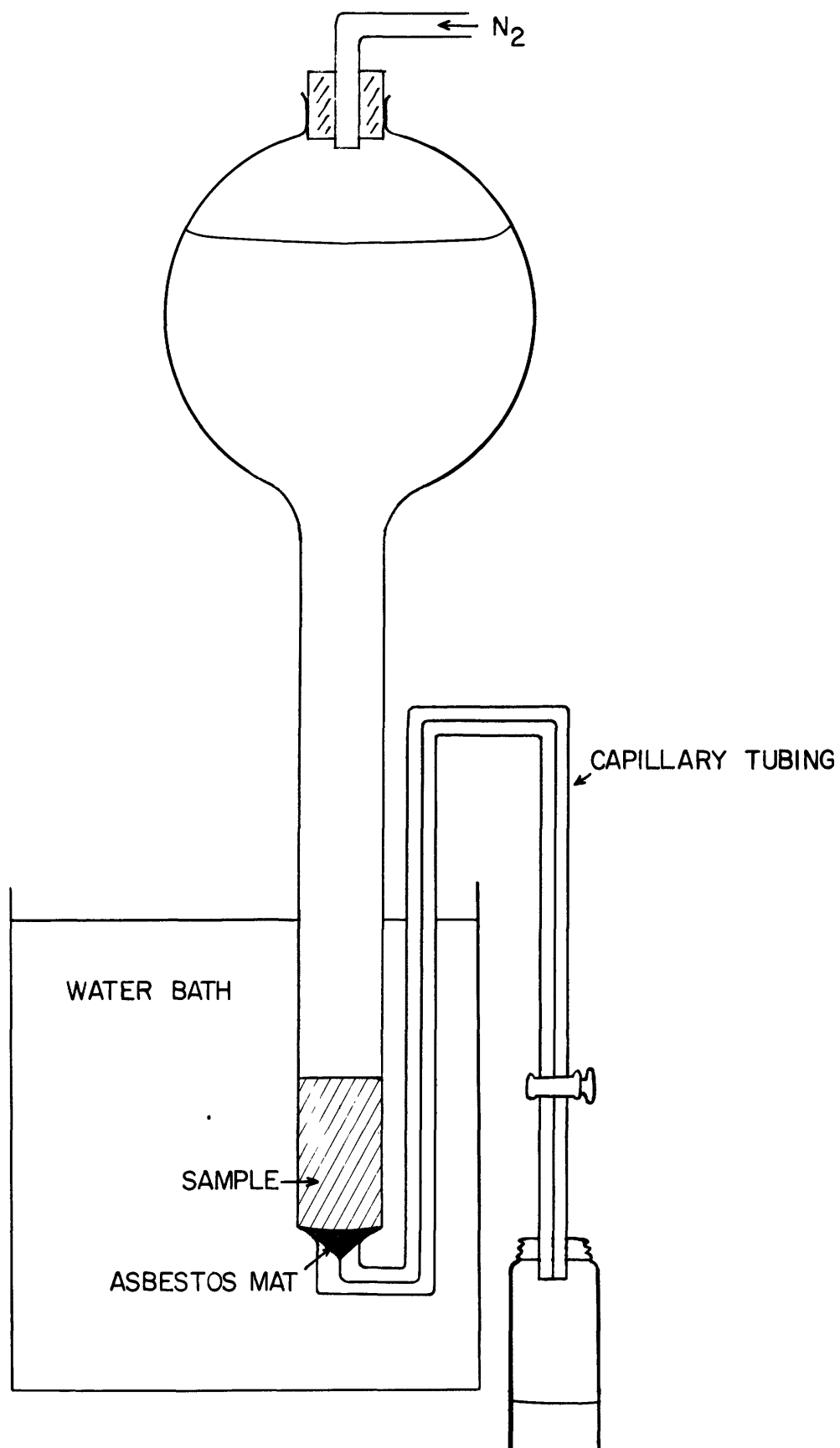


FIGURE 1. SORPTION APPARATUS

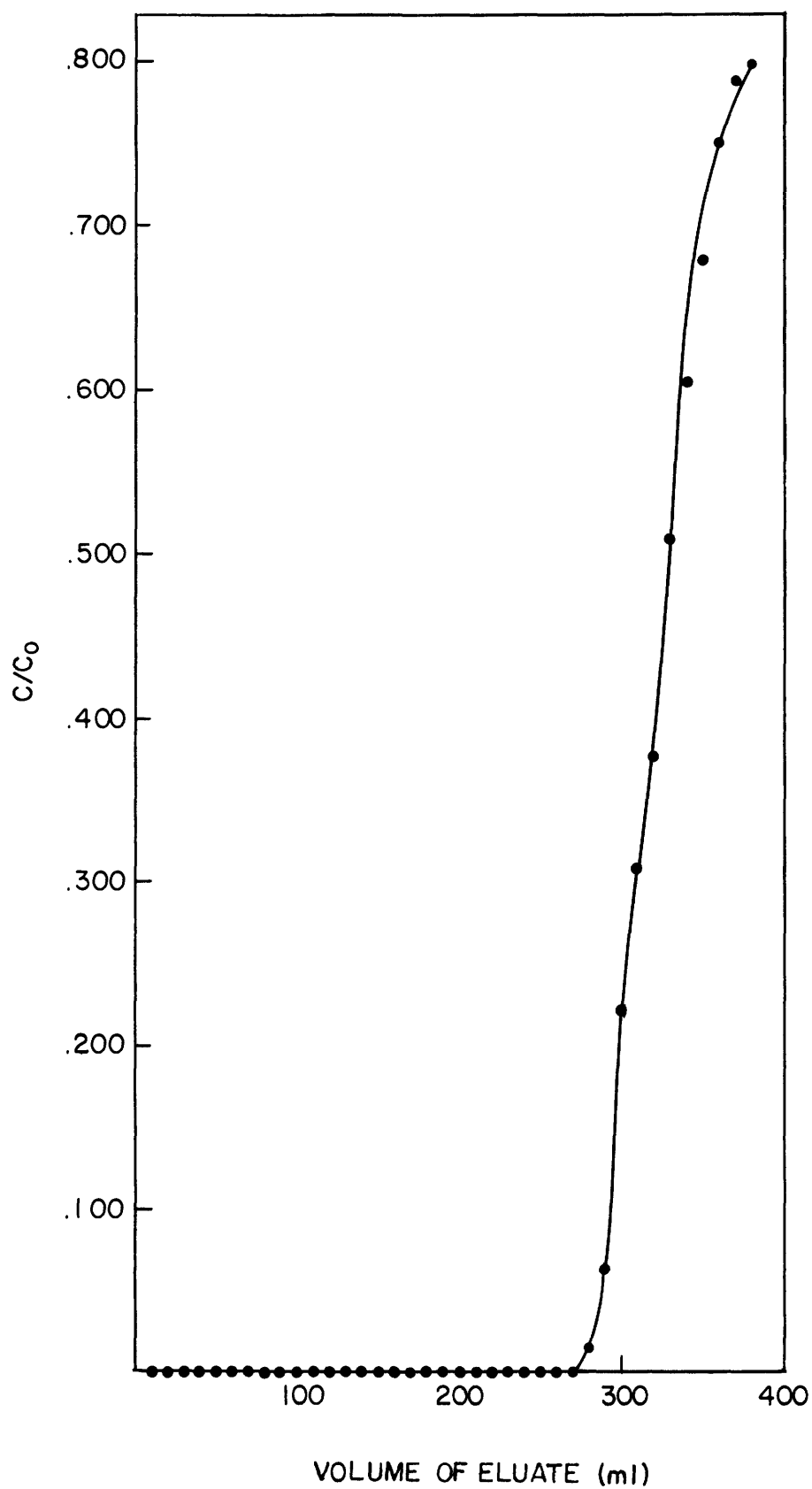


FIGURE 2. SORPTION OF STRONTIUM BY 40g OF CRANDALLITE ORE (+ 35 mesh fraction):
 $C_0 = 100 \text{ ppm Sr.}$

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Determinations of P_2O_5 , made on representative fractions of eluate, gave a P_2O_5 range from 50 to 100 ppm, indicating solubility of phosphatic material under these conditions or the hydrolytic evolution of phosphate.

In view of the well-known incongruous solubility of the basic calcium phosphates, the conditions of this experiment would probably favor the formation of an apatite-like phase, $A_{10}(XO_4)_6(OH)_2$, rather than a less basic compound. This follows from the hydrolysis behavior of calcium phosphates in which compounds more acid than apatite (including tricalcium phosphate $A_3(XO_4)_3$) tend to hydrolyze to the stable apatite form with liberation of excess phosphoric acid.

The subsequent experiments were performed with a representative split of the sample which was gently crushed. The particle size distribution of the crushed material was as follows: less than one percent coarser than 20 mesh, 16 percent in the -20 to +35 range, 61 percent in the -35 to +100 range, and 23 percent finer than 100 mesh.

The sample was sufficiently fine to enable the use of 12-mm diameter columns without channelling problems. However, to facilitate a good rate of flow the sample was usually blended with twice its weight of 80- to 100-mesh acid-washed silica sand. Feed solutions contained 50 ppm Sr and were spiked with Sr^{89} .

A check of the strontium sorption of 4 grams of the silica sand and 18 mg of asbestos indicated that the uptake of the blank was insignificant.

The effect of pH on the strontium uptake was studied in column experiments using buffered and unbuffered solutions with one or two grams of crandallite (table 2). The solution was buffered at pH 3 by adding 0.05 moles of sodium acetate and hydrochloric acid per liter (fig. 3). The solutions buffered at approximately pH 6 were 0.005M with respect to sodium dihydrogen phosphate, the pH being adjusted with dilute sodium hydroxide solution. Inasmuch as phosphate was dissolved in small amounts from the sample by mildly acidic and alkaline solutions, the presence of added phosphate did not represent a drastic change in the system.

Flow rates of approximately 10 ml per 15 minutes (0.6 ml/min/cm^2) were maintained, when possible, by partly closing the stopcock or by applying external pressure. In most of the experiments made with solutions ranging from pH 5 to pH 8, slow flow rates required the application of as much as 7 psi of nitrogen to maintain the desired flow. Even with the application of pressure, however, some flow rates were much less than 10 ml per hour; experiments with very slow flow rates were discontinued after approximately one day.

At pH 6, the strontium uptake is the same, within the experimental error, for the buffered and unbuffered solutions (fig. 4, table 2). As anticipated the unbuffered solutions, especially those with pH values differing considerably from the equilibrium pH of the crandallite, underwent a large change in pH; this was most pronounced in the first eluate fractions.

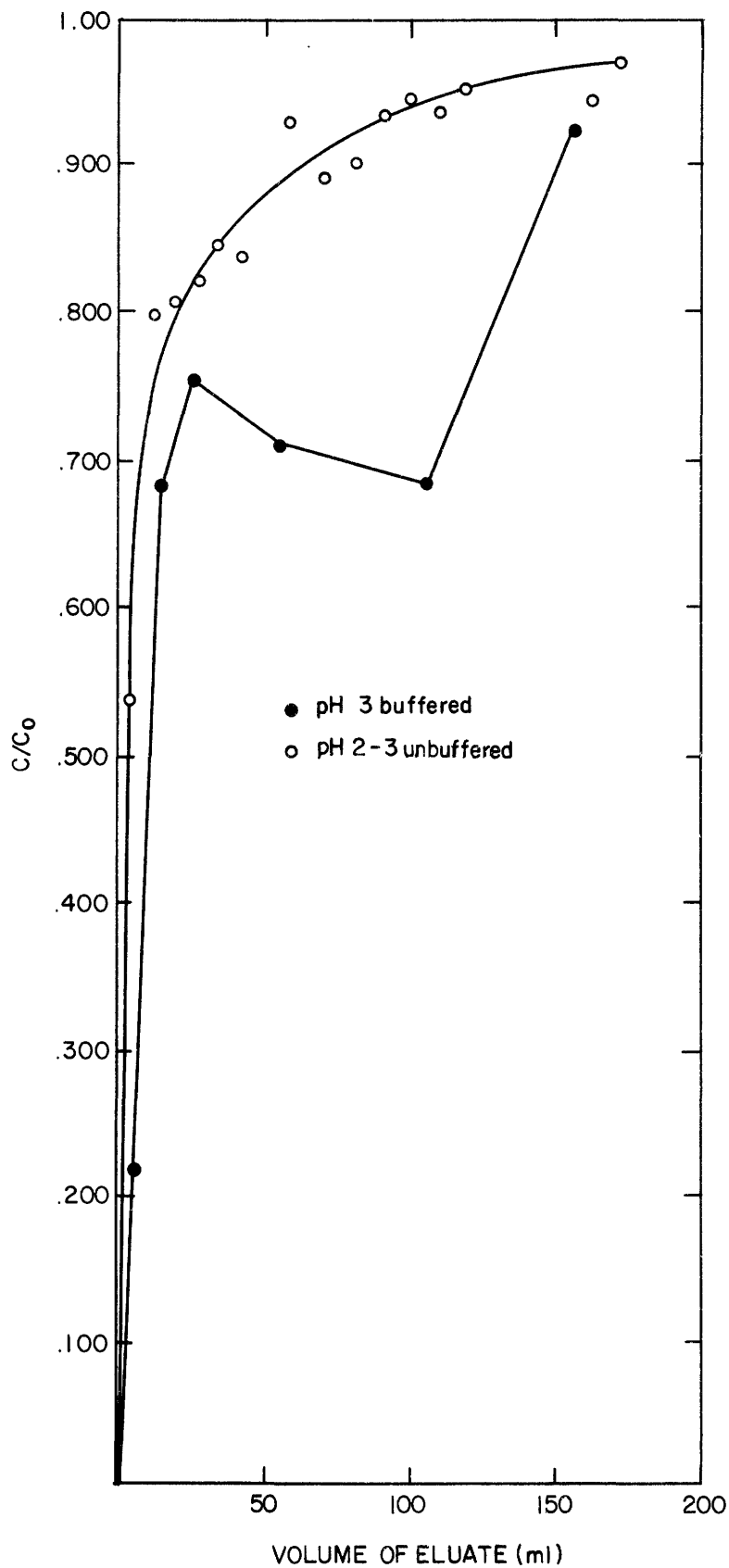


FIGURE 3. STRONTIUM REMOVAL FROM SOLUTIONS AT pH 3 BY CRANDALLITE:
 $C_0 = 50$ ppm Sr.

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Marked trends are apparent in the total strontium uptake as a function of pH, although it is recognized that strict comparisons may not be justifiable because of variations in volumes of feed solution and in contact time. The total observed strontium uptake from unbuffered solutions at pH 3, 6, and 10.5 were 1, 6, and 27 meq Sr/100 grams, respectively. It is of interest to compare these values with the total exchange capacity values of 0.3, 1.5 and 8.5 meq Sr/100 grams derived from the 50 percent break-through capacities. The relatively large difference between corresponding capacities suggests a precipitation reaction occurring simultaneously with the sorption. At high pH values the precipitation reaction predominates, a precipitate forming as a discrete layer on the column bed.

It may be concluded from the column experiment data that the differences in the experimental and calculated uptake represent the amount of precipitation. It is apparent that this difference increases with pH.

In the region of pH 3 there is relatively little removal of strontium from buffered or unbuffered solutions. As shown in figure 3 even the first 10 ml of eluate contain strontium and the C/C_0 values thereafter rise sharply.

In the pH range of 5-6 the strontium uptake from feed solutions was greater than at pH 3. With increasing pH there is not only an increase in break-through capacities but a more gradual rise in the C/C_0 values, the curve tending to flatten at values lower than 1.0. The phosphate buffer does not alter significantly the strontium-uptake capacity of the system.

At pH 10.5 strontium uptake is greater than at lower pH values (fig. 5); the C/C_0 value never exceeded 0.7. The strontium capacity of the column charge was partly regenerated after standing overnight.

Experiments were made at 30° and 55°C with one gram portions of crandallite and a solution at pH 6 to determine the temperature effect on the strontium uptake (fig. 6). The strontium sorption did not differ significantly for these two temperatures, being 5.5 and 5.7 meq Sr/100 grams respectively.

Experiments were also made with solutions having the approximate alkali content of tank-supernatant liquid of a typical alkali-treated Savannah River waste solution. The solution used was 0.46 M with respect to sodium hydroxide and had 18.3 ppm Sr. In a column experiment with a one gram charge of crandallite all the strontium was removed from the first 30 ml of feed solution; that is, the break-through capacity equalled 550 μ g Sr (fig. 7). The C/C_0 value then rose as high as 0.6-0.7 at the end of the day's run of 280 ml of solution. After a night's interruption, the next 60 ml of eluate had C/C_0 values no higher than 0.007 and then rose slowly during the day to a maximum of 0.45. Again the C/C_0 value dropped off overnight to 0.004 (total volume of the eluate at this point was 560 ml). The P_2O_5 content of the eluate fractions was inversely related to the strontium content. The P_2O_5 value of the fractions collected at the start of the run after each night's interruption exceeded 200 ppm. In other fractions the P_2O_5 content ranged from 15-120 ppm.

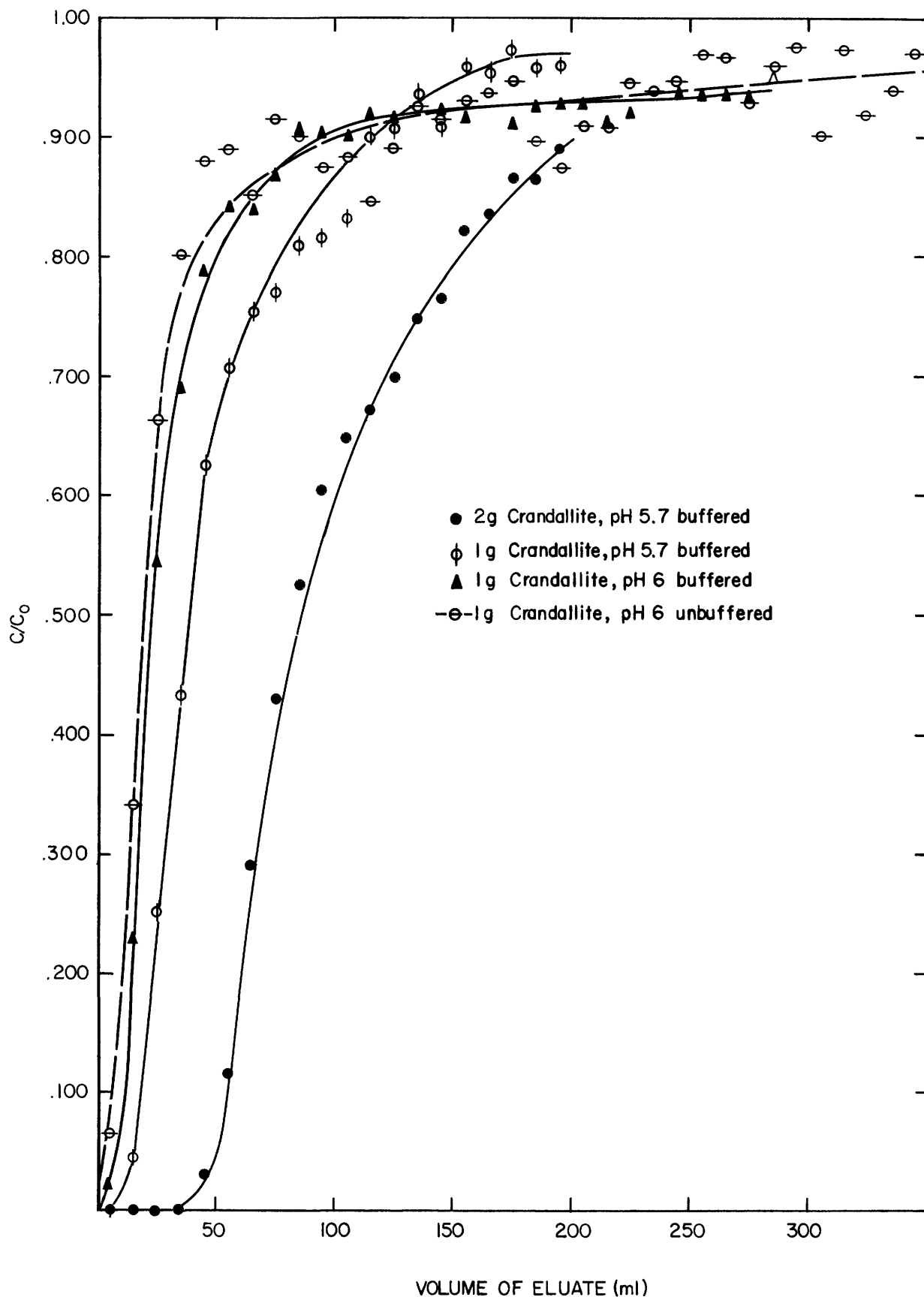


FIGURE 4. STRONTIUM REMOVAL FROM WEAKLY ACID SOLUTION
BY CRANDALLITE: $C_0 = 50$ ppm Sr.

Table 2.--Summary of column experiments; pH range 2-10

Crandallite : sample weight (g)	Contacting solution		Average : flow rate : (ml/min/cm ²)	Total uptake : meq/100 g	Figure
	Total volume :	pH			
	: of eluate (ml)	: Buffered : unbuffered : exp. 1/ : calc. 2/			
Strontium 50 ppm					
2	222	---	2-3	3/ 0.94	3
2	180	4/ 3	---	3/ 2.7	3
1	200	5/ 5.7	---	6/ 6.3	4
2	200	5/ 5.7	---	6/ 5.8	4
1	290	5/ 6.0	---	6/ 5.5	4,6
1	380	---	6.0	6/ 5.5	4
1	290	5/ 6.0	---	7/ 5.7	6
1	270	5/ 5.5	---	7/ 6.6	---
1	470	---	10.5	6/ 27.0	5
Cesium 50 ppm					
1	80	5/ 6.0	---	6/ 1.4	9
1	210	---	6.0	6/ 1.6	9

1/ Experimental uptake--total decrease in strontium content of the feed solution after passing through the column.

2/ Calculated uptake--value obtained from the abscissa corresponding to the point $C/C_0 = 0.5$.

3/ Room temperature.

4/ Buffer--sodium acetate and hydrochloric acid (0.05 moles of each per liter).

5/ Buffer--sodium dihydrogen phosphate (0.005M + NaOH).

6/ Experiment made at 30°C with the aid of a thermostatically controlled water bath.

7/ Experiment made at 55°C with the aid of a thermostatically controlled water bath.

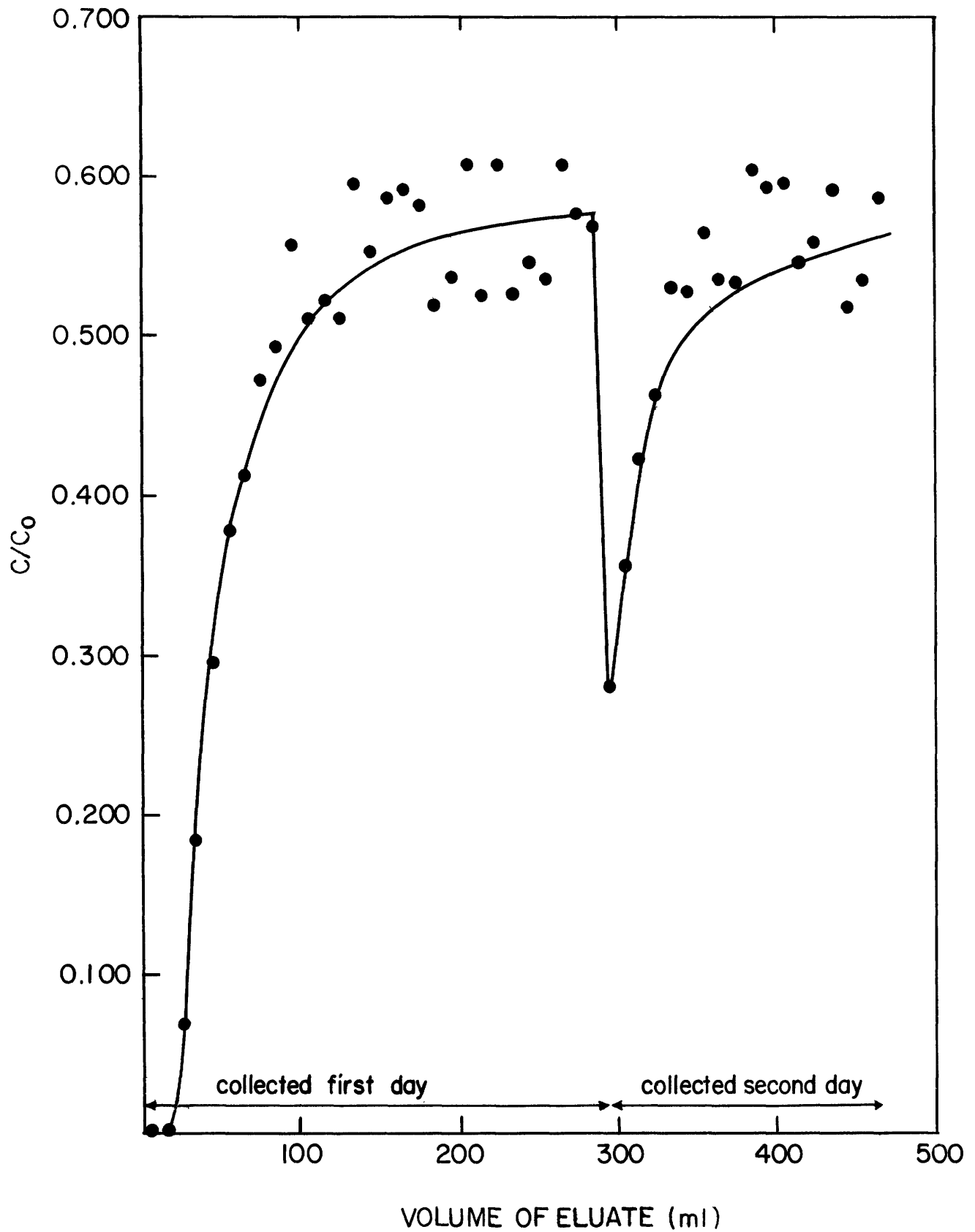


FIGURE 5. STRONTIUM REMOVAL FROM SOLUTION AT pH 10.5 BY CRANDALLITE: $C_0 = 50$ ppm Sr.

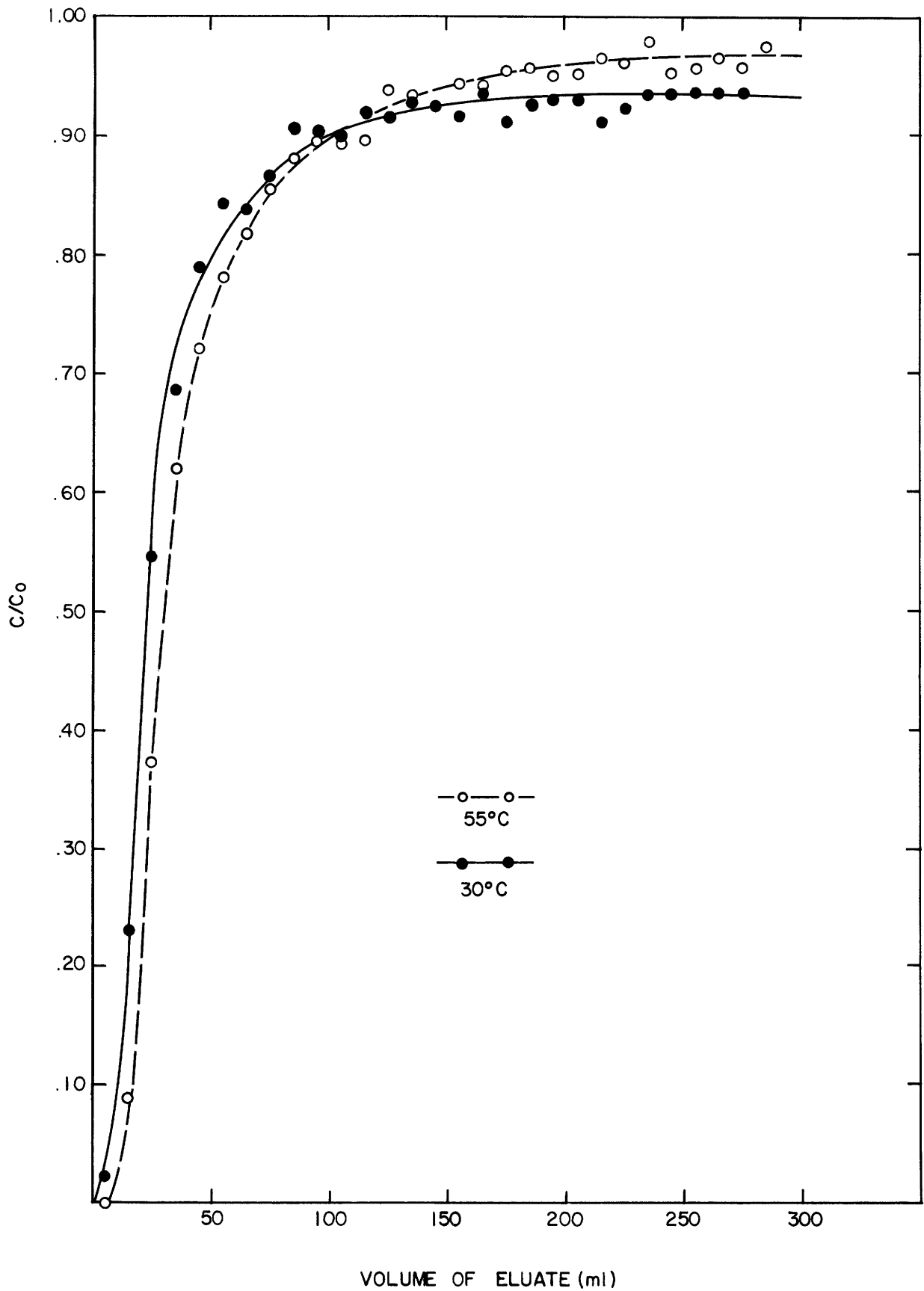


FIGURE 6. TEMPERATURE EFFECT ON STRONTIUM REMOVAL BY CRANDALLITE FROM SOLUTIONS BUFFERED AT pH 6 (phosphate buffer);
Co = 50ppm Sr.

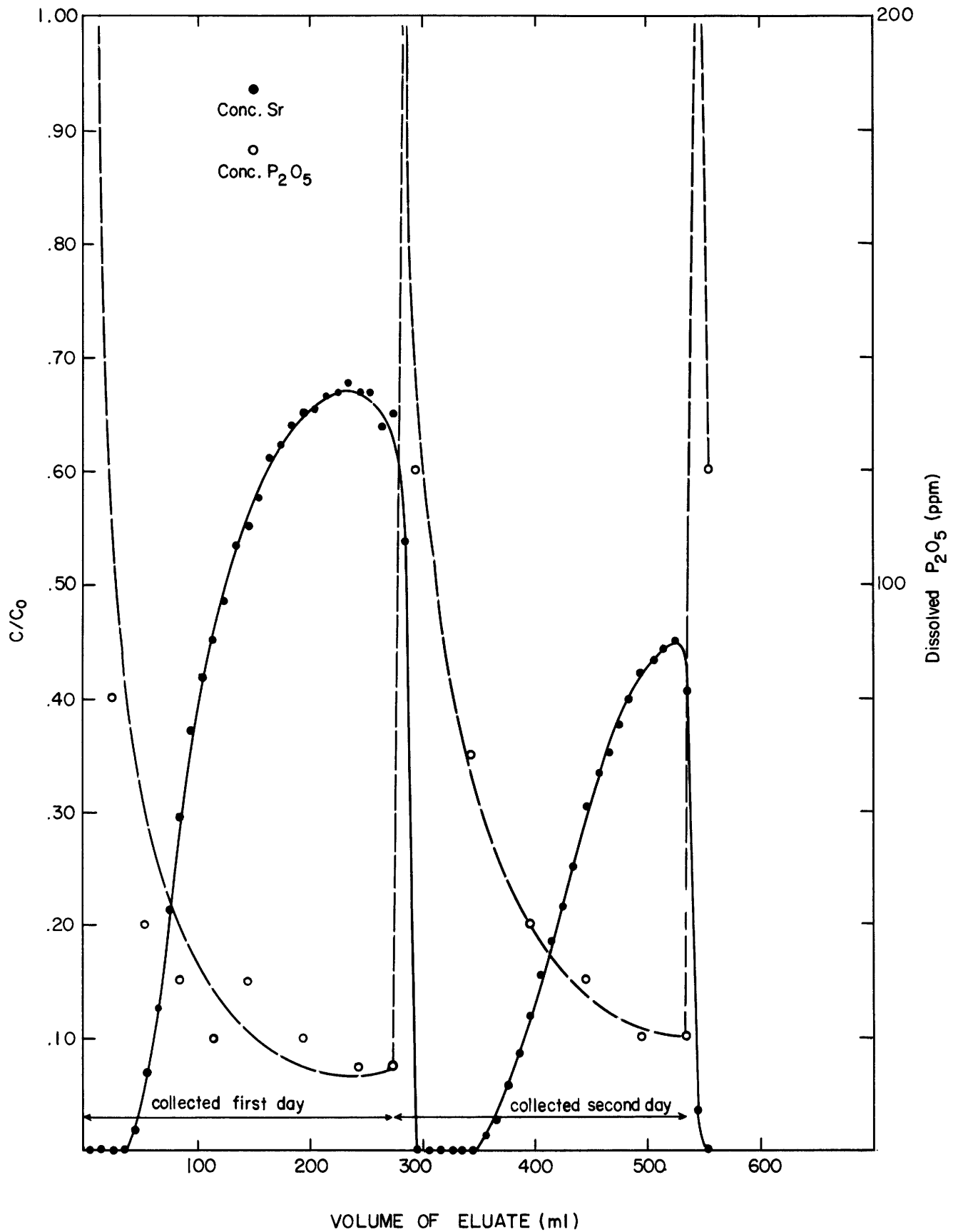


FIGURE 7. STRONTIUM REMOVAL FROM AND PHOSPHATE SOLUTION IN 0.46M NaOH WITH CRANDALLITE: $C_0=18.3$ ppm Sr.

A precipitate was clearly discernible on the upper surface of the column bed. Although it was not possible to isolate it completely from the crandallite packing, some identification tests were attempted; the results were not wholly conclusive. Infra-red tests by Irving Breger, U. S. Geological Survey, could not establish the presence of strontium carbonate nor strontium orthophosphate. X-ray examination by Marie Lindberg, U. S. Geological Survey, showed the presence of apatite and quartz and a strong 2.90-2.91 Å reflection from Cu-K α radiation (possibly crandallite reflection); broad reflections were obtained indicative of poor crystallinity. It is likely that the strontium was present in the material having the structure of apatite. This is consistent with the findings of Denk and Boppel (1961) who have recently reported the formation of apatite phases in the precipitation of strontium phosphate under similar conditions.

Aluminum is frequently present in nuclear wastes. Therefore a column experiment was made to determine the effect of aluminum on crandallite's removal of strontium from a solution 0.5M with respect to sodium hydroxide (fig. 8). A 50-ppm strontium solution spiked with strontium-89 was prepared containing 0.33 mg aluminum per ml in the form of sodium aluminate. Flow rates averaging 0.3 ml/min/cm² were maintained; only at the latter part of the experiment was it necessary to apply 0.5 psi pressure to maintain this flow rate. A precipitate formed at the top of the column bed. A concentration of the radioactivity in the precipitate was readily determined with a portable monitor. The C/C₀ values rose gradually after the first 30 ml of eluate, reached a maximum of 0.2 after the passage of 130 ml of eluate, and then decreased with additional feed solution as the day's run progressed. The C/C₀ values of the eluate for the next 2 days (170 ml) remained less than 0.002. A total of 370 ml of eluate were collected from which 14.3 mg of strontium were removed or 32.5 meq Sr/100 grams. Again, as with experiments at this alkalinity in the absence of aluminum, precipitation of strontium appears to be the predominant reaction.

Batch experiments

Batch experiments were also made with strontium. Half-gram samples of crandallite were treated for 19 hours at room temperature with 10, 25, and 100 ml of 50 ppm strontium solution at pH 8.3. The percentages of strontium removed were 89, 65, and 31, respectively. The strontium concentration in the residual solutions ranged from 5 to 35 ppm even though there was a tenfold increase in the strontium in contact with a fixed sample weight.

A test of the concentration effect of strontium was made by treating quarter-gram portions of crandallite ore for 48 hours at room temperature with 50 ml volumes of 0.5M sodium hydroxide solutions containing varying concentrations of strontium. Strontium concentrations ranging from 2 to 50 ppm were reduced to 0.01-0.03 ppm.

Another batch experiment was made to determine the rate of the strontium removal from solution by the crandallite ore. Ninety-nine percent of the strontium is removed within one hour and 99.9 percent in 16 hours (table 3). The total strontium uptake corresponds approximately to that calculated from a column experiment with strontium solution at pH 10.5 (table 2).

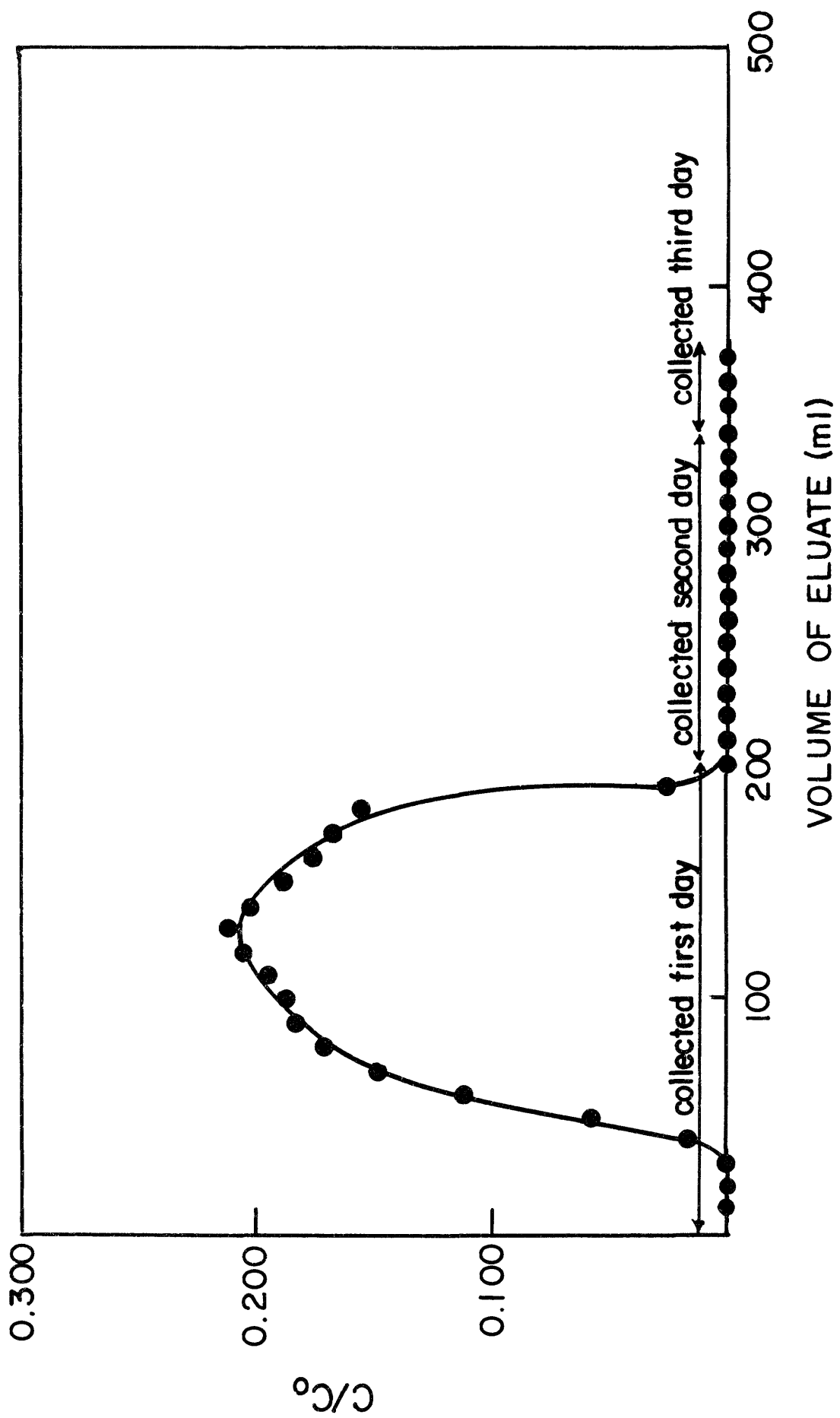


FIGURE 8. STRONTIUM REMOVAL BY CRANDALLITE IN THE PRESENCE OF ALUMINUM: $C_0=50$ ppm Sr

Table 3.--Rate of strontium removal by 0.2500 g of crandallite from 25 ml of 50 ppm Sr in 0.5 M NaOH

<u>Contact time</u> <u>(hr)</u>	<u>Residual Sr</u> <u>(ppm)</u>	<u>Total uptake</u> <u>(meq Sr/100 g)</u>
1	0.58	11.2
2	0.30	11.3
4	0.20	11.3
16	0.02	11.4
256	0.07	11.3

SORPTION OF CESIUM

As cesium is a constituent of radioactive wastes it was desirable to determine the extent crandallite would remove cesium from solution. Column experiments were made with one-gram crandallite charges using 50 ppm cesium solutions spiked with cesium-137 ($0.02 \mu\text{c/ml}$) both buffered and unbuffered at pH 6. The count of the feed solution was approximately 700 times the background level. The activity of the eluate was measured with a sodium iodide crystal scintillation counter. The unbuffered solution gave flow rates averaging 0.7 ml/min/cm^2 without the application of external pressure. However, the buffered solution required 5 psi pressure even to maintain the slow flow rate of 0.07 ml/min/cm^2 . The cesium appeared in the first 10 ml of eluate collected in each case and the C/C_0 values climbed rapidly thereafter (fig. 9). The pH of the unbuffered eluate ranged from 6.2 to 6.9 and that of the buffered eluate from 5.5 to 6.1. The total volumes of eluate collected from the unbuffered and buffered solutions were 210 and 80 ml, respectively, giving exchange capacities of 1.6 and 1.4 meq Cs/100 grams.

A column experiment with cesium was also made using a 50 ppm Cs solution in 0.5 M sodium hydroxide and one gram of crandallite. The flow rate averaged 0.3 ml/min/cm^2 without the application of pressure. The first 10 ml eluate fraction had a C/C_0 value of 0.6; the C/C_0 values then rose steeply to 1.0. The total exchange capacity equalled 0.2 meq Cs/100 ml. The results indicate that the sodium ions offer serious competition to the exchange reaction of cesium with crandallite.

In a batch experiment quarter-gram portions of crandallite were treated with varying volumes of 50 ppm cesium solution buffered at pH 6. The solution volumes were 10, 25, 50, and 100 ml. After approximately 24 hours of contact time at room temperature the supernatant liquids were removed and their cesium content determined (table 4). The pH of the supernatant liquid did not change. The data suggest the probability of an exchange rather than a precipitation mechanism. It can be seen that crandallite has a low exchange capacity for cesium.

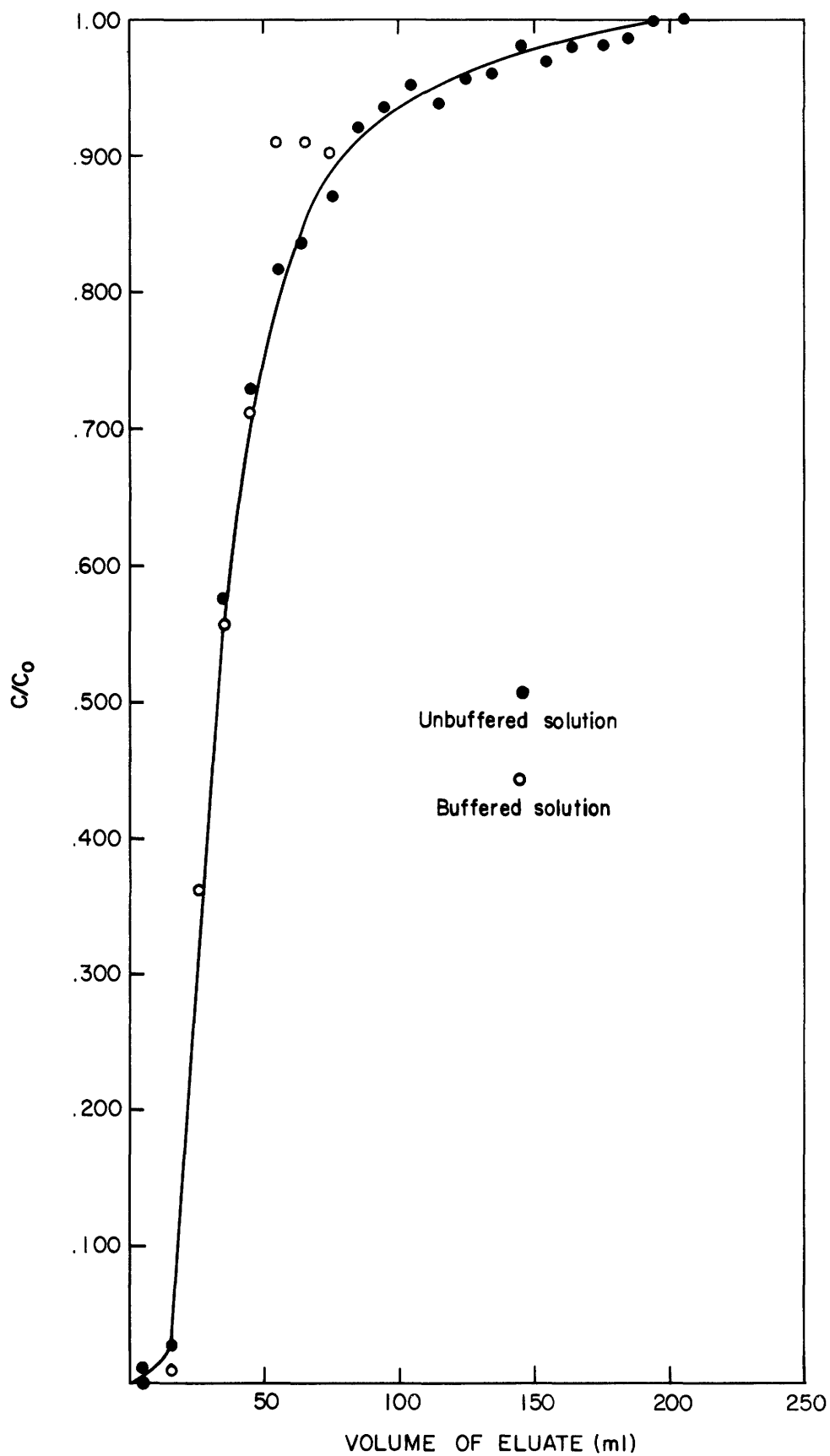


FIGURE 9. CESIUM REMOVAL FROM SOLUTIONS AT pH 6 BY CRANDALLITE: $C_0=50$ ppm Cs

Table 4 --Cesium sorption by 0.2500 g crandallite from varying volumes of 50 ppm Cs solution buffered at pH 6

<u>Solution volume (ml)</u>	<u>Residual Cs (ppm)</u>	<u>Total uptake (meq Cs/100 g)</u>
10	22	0.83
25	35	1.1
50	41	1.3
100	45	1.5

SUMMARY

Break-through curves obtained in column experiments with crandallite and mildly acid strontium solutions indicate the occurrence of an ion exchange reaction. Strontium removal is many times more effective from alkaline solutions, precipitation being the dominant mechanism. The removal of strontium is even more complete in alkaline solutions containing aluminate ions.

As expected, crandallite is much less effective in the removal of cesium, primarily owing to the absence of a precipitation reaction. The exchange capacity of the crandallite sample studied is not very high, being 6-10 meq Sr and 2 meq Cs per 100 grams of active phosphatic material.

Crandallite ores may be useful in the treatment of nuclear waste solutions because of their reactivity with strontium in weakly acid solutions and in alkaline solutions containing aluminum.

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